

# Rheology of nanofibrillated cellulose/acrylate systems for coating applications

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**Abstract** In this work, the suitability of nanofibrillated cellulose (NFC) as a novel component for wood coatings has been evaluated. NFC was prepared from two different wood pulps with a high pressure homogeniser and a grinder, depending on the initial fibre size of the two pulps. The fibrillation process was monitored using viscosity measurements and scanning electron microscopy. Viscosity measurements were found to be a suitable, reliable and especially fast and easy method for process monitoring, optimization and quality assessment of the NFC fibrillation process. NFC was mixed with four different waterborne acrylic polymer emulsions and analysed regarding its rheological behaviour. The viscosity of the acrylate–NFC suspensions was dominated by the NFC, whereas the polymer type was of minor importance at the tested concentrations. The viscosity increased exponentially after NFC addition and consequently the viscosity of such suspensions would be precisely adjustable in the considered shear range. During accelerated storage at elevated temperatures, the general flow behaviour did not change; only a slight viscosity increase was observed. The study shows that rheology is an important issue that has to be taken into account when

applying NFC as additive in water based coating systems and that NFC is suitable as component for coating applications.

**Keywords** Nanofibrillated cellulose · Rheology · Acrylate emulsion · Waterborne · Coating application

## Introduction

When used for outdoor applications, the biomaterial wood is exposed to UV radiation, rain and humidity, mechanical impacts and microorganisms (Wicks et al. 2006). All these effects can degrade the wood surface, decrease its durability and change its appearance. Protective coatings are thus necessary to avoid premature and expensive maintenance. Main components of coatings are polymeric binders among which waterborne polymer emulsions such as acrylates are attracting more and more interest (Philipp 2010). The trend to waterborne systems is obvious, as toxic volatile organic components (VOC) and thus flammability are reduced and more environmentally friendly products are produced.

The performance and durability of organic wood coatings is expected to be improved by nanofibrillated cellulose (NFC) as novel additive, which would act as mechanically reinforcing component and as carrier for functional agents such as UV absorbers or antimicrobials.

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Nanofibrillated cellulose and other nanocelluloses have already been reported widely as reinforcing components for polymers (Dufresne 2012). Using nanocelluloses is attractive because of their beneficial properties: they exhibit excellent mechanical performance at low weight, are biocompatible, transparent and reactive due to the hydroxyl groups on their large fibre surfaces (Klemm et al. 2011). Nanocelluloses derive from cellulose, a renewable, biodegradable and the most abundant biopolymer on earth. NFC has already been isolated from many different cellulose materials such as wood pulp, hemp, sugar-beet pulp and others (Zimmermann et al. 2010; Helbert et al. 1996; Agoda-Tandjawa et al. 2010). The first isolation of NFC from wood cellulose pulp was carried out with a homogenizer and was described by Turbak et al. (1983). Nowadays, different mechanical isolation procedures have been established. High-shear homogenizers and grinders are the most favoured methods (Zimmermann et al. 2004; Iwamoto et al. 2005). In addition, chemical or enzymatic pre-treatments of cellulose pulps were introduced to shorten the isolation process and to minimize energy consumption (Saito et al. 2006; Pääkkö et al. 2007). In such ways, fibres with diameters between 5 and 100 nm and lengths of more than 1  $\mu\text{m}$  are produced.

For the preparation of nanocellulose nanocomposites, a wide range of polymers has already been tested, e.g., polylactic acid, hydroxypropyl cellulose, polyvinylacetate, polyacrylate latices and epoxy resin (Favier et al. 1995; Ruiz et al. 2001; Tingaut et al. 2010; Lopez-Suevos et al. 2010). Different applications of such nanocomposites were proposed and examined, e.g., in biomedicine, for packaging materials and for electronic displays (Eyholzer et al. 2011; Ho et al. 2012; Yano et al. 2005). Few researchers also mentioned the potential use of nanocelluloses in coating materials and examined NFC containing coatings for the paper and packaging industry (Ruiz et al. 2001; Cavaille et al. 2000; Martins et al. 2012; Ridgway and Gane 2012; Aulin and Ström 2013). There, the addition of NFC targets material improvements related to barrier, antimicrobial and mechanical properties and processing characteristics. However, reports on using nanocelluloses in wood coatings are rare. Landry and Blanchet (2009) used silane modified nanocrystalline cellulose to produce hydrophobic wood coatings and Jämsä et al. (2010) used NFC to achieve a better distribution of nanoparticles within wood coatings.

Apart from the mentioned functions of NFC in coatings, rheological effects are very important for coating processing and application. For instance, a higher viscosity is required for roller coating than for spray coating applications and a too high viscosity would cause insufficient levelling of the coating on the substrate (Bulian and Graystone 2009).

The first rheological study on NFC was published in the pioneering works by Herrick et al. (1983), who described the shear thinning behaviour of a suspension of 2 % (w/w) NFC in water. This has been explained later by the breakdown and the change of the inner structure of NFC suspensions (Iotti et al. 2011; Karppinen et al. 2012). It is also well known that NFC suspensions exhibit higher viscosities with advanced fibrillation grade or increasing NFC concentration (Saito et al. 2006; Saarikoski et al. 2012). During fibrillation, the surface area increases and therefore more interactions between fibres and fibril aggregates, considered as flocs, are possible, which leads to higher resistance to flow. The influence of temperature, pH and salts on the flowing properties of NFC suspensions was further investigated. By changing the temperature, only slight viscosity changes were monitored. However, the viscosity increased at decreasing pH or increasing salt concentration due to the reduction of interfibrillar, electrostatic repulsion at higher hydrogen ion or salt concentration (Pääkkö et al. 2007; Agoda-Tandjawa et al. 2010). Moreover, low amounts of water-soluble polymers such as sodium carboxymethylcellulose and sodium polyacrylate were added to nanocellulose suspensions (Lows et al. 2001; Boluk et al. 2012). There, the viscosity of a suspension of cellulose nanocrystals (CNC) with Newtonian flow behaviour was increased and changed to shear thinning flow after polymer addition.

To our knowledge, only two reports exist about viscosity measurements of polymer emulsions containing nanocellulose materials. Ruiz et al. (2001) described a suspension of a waterborne epoxy polymer emulsion and CNC designated for coatings without mentioning a specific application. The nanocrystals significantly increased the viscosity compared to the neat epoxy emulsion at low shear rates. At higher shear rates (100 l/s) the viscosity was nearly the same for the neat polymer emulsion and the polymer-CNC suspension. Bousfield et al. (2013) prepared suspensions containing NFC, carboxylated styrene-butadiene latex and kaolin clay. They showed increasing

viscosities with increasing amounts of NFC at constant polymer and kaolin contents and the suspensions had the typical shear thinning behaviour of neat NFC suspensions. However, until now, no information about the rheology of NFC and acrylate suspensions is available.

Aim of this work was therefore to investigate changes of rheological properties of water-borne acrylate suspensions by the addition of NFC, with regard to coating applications.

## Materials and methods

### Materials

Two never dried cellulose raw materials were chosen, namely a refined fibrous beech wood pulp with 79 % cellulose content, 14 % hemicelluloses and 0.8 % rest lignin (Arbocel<sup>®</sup>, J. Rettenmeier & Söhne GmbH&Co. KG, Germany) and a totally chlorine-free softwood kraft pulp with 81 % cellulose content, 14 % hemicelluloses and 1.5 % rest lignin (TCF, Zellstoff Stendal, Germany). The chemical composition of the pulps was determined according to TAPPI standards. Four different commercially available binders in form of acrylate polymer emulsions were selected to prepare the acrylate–NFC suspensions. Table 1 presents the four polymer emulsions including their suppliers and their properties as declared by the suppliers. The additives used and their corresponding suppliers are included in Table 2.

### Fibrillation of cellulose raw materials

The two cellulose raw materials were fibrillated by using different mechanical processes, which are schematically shown in Fig. 1. The beech wood pulp was

suspended in deionized water to obtain a suspension of 1.5 % (w/w) concentration. The suspension was continuously stirred at 10 °C for at least 4 days to enable swelling. The swollen pulp was treated in an inline dispersing system (Megatron MT 3000, Kinematica AG, Switzerland) at 16,000 rpm for 25 min/kg suspension. Then, the suspension was processed in a high pressure homogenizer (Microfluidizer<sup>®</sup>, Microfluidics Corporation, USA) with two interaction chamber combinations and pressures up to 1,200 bar. First, the suspension was passed 10 times through chambers with diameters of 400 and 200 µm (H230z, H30z). Afterwards, the suspension was diluted to 1.3–1.4 % (w/w) due to viscosity increase and then was passed 10 times through chambers with diameters of 200 and 75 µm (H30z, F20y). The resulting NFC material is further named NFC1.

The softwood pulp was first disintegrated in a grinder (Supermasscolloider MKZA 10–20 J CE,

**Table 2** Standard formulations of acrylate–NFC1 suspensions with 0.25 % (w/w) NFC content

Component	Content in suspension [%]			
	Acr1	Acr2	Acr3	Acr4
Polymeric binder (solid content)	25	25	25	25
NFC1 (solid content)	0.25	0.25	0.25	0.25
Defoamer	0.5 <sup>a</sup>	0.5 <sup>a</sup>	0.5 <sup>b</sup>	0.5 <sup>b</sup>
Wetting agent <sup>c</sup>	0.2	0.2	0.2	0.2
Film forming agent <sup>d</sup>	–	–	–	2.85
Deionized water	74.05	74.05	74.05	71.2
Sum	100	100	100	100

<sup>a</sup> TEGO Foamex 822 (Evonik Tego Chemie GmbH, Germany)

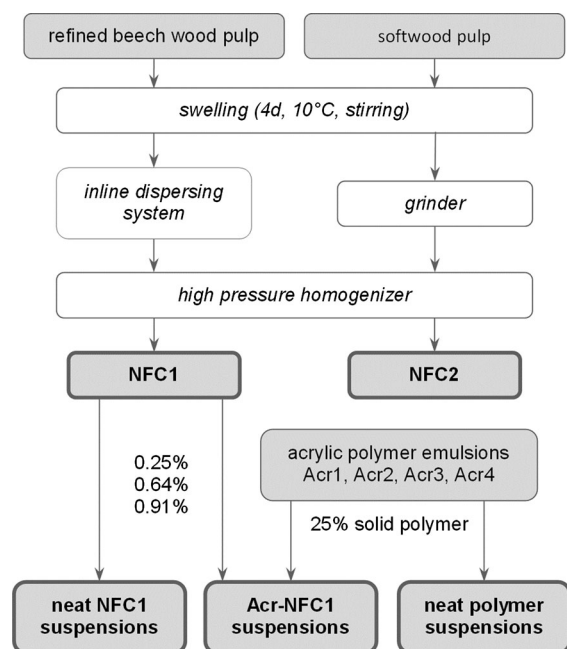
<sup>b</sup> BYK-028 (BYK Additives & Instruments, Germany)

<sup>c</sup> BYK-348 (BYK Additives & Instruments, Germany)

<sup>d</sup> Butyl glycol (Alfa Aesar, USA)

**Table 1** Types and suppliers of used acrylate polymer emulsions (binders)

Acronym	Commercial name	Supplier	Polymer and stabilization	Solid content [%]
Acr1	Alberdingk AC 2739	Alberdingk Boley GmbH, Germany	Acrylic acid/methacrylic acid co-polymer emulsion, surfactant free	44–46
Acr2	Acronal DS 6288	BASF SE, Germany	Anionic, acrylic emulsion	44
Acr3	Mowilith LDM 7416	Celanese, USA	Acrylic acid/methacrylic acid styrene co-polymer, anionic surfactants	49–51
Acr4	NeoCryl XK-98	DSM N.V., Netherlands	Anionic, acrylic co-polymer emulsion	44



**Fig. 1** Schematic overview of NFC disintegration processes and sample preparation for rheology measurements; intermediate sampling for quality and fibrillations process control is not included

Masuko Sangyo Co. Ltd., Japan). This was necessary because the pulp fibres were too long and therefore clogged the inline dispersing system used for the pre-treatment of the other raw material. A softwood pulp suspension of 2 % (w/w) in deionized water was prepared and premixed using a blender. After swelling it for 4 days at 10 °C under constant stirring, the suspension was passed through the grinder 10 times. After seven passes, the suspension was diluted with water to 1.8 % (w/w) to decrease viscosity. In the second step, the suspension was transferred to the high pressure homogenizer, diluted to 1.5 % (w/w) and processed as described before for the NFC1. The resulting NFC material is named NFC2.

Both NFC suspensions were concentrated by centrifugation for storage in the fridge.

#### Preparation of acrylate–NFC1 suspensions

Acrylate–NFC1 suspensions were prepared according to a standard coating formulation based on the suppliers' recommendations (Table 2). For all suspensions, a constant acrylic polymer solid content of 25 % (w/w) was used. NFC1 concentration was varied

from 0.25 over 0.64 to 0.91 % (w/w) in the suspension to achieve concentrations of 1, 2.5 and 3.5 % of dry NFC1 referred to the solid polymer. These are typical concentrations for coating additives. Some essential additives for processing were added to the suspensions, such as a defoamer, to minimize foaming during processing, a wetting agent to have a better substrate wetting, and a film forming agent. Table 2 shows the standard formulation of acrylate–NFC1 suspensions with 0.25 % (w/w) NFC content and the different additives used depending on the acrylate raw materials.

For suspension preparation, the acrylate polymer emulsions were first diluted with the calculated amount of water and the additives were added while stirring with a dissolver stirrer. The NFC1 was added in form of the concentrated suspension obtained as described above. The suspensions were stirred for 30 min and stored at 20 °C. As depicted in the schematic overview in Fig. 1, neat NFC1 suspensions at the same NFC concentrations and reference polymer suspensions containing the polymer and the additives without NFC were prepared as well.

#### Characterization

##### *Degree of polymerization (DP)*

The limiting viscosity number  $[\eta]$  of the used cellulose raw materials and the NFC thereof were determined according to ISO 5351 (ISO 2004). Beech wood pulp, softwood pulp, NFC1 and NFC2 were first dried via freeze drying and afterwards in the oven at 50 °C for at least 24 h. Depending on the assumed DP, a defined amount of material was dissolved in cupri-ethylene-diamine solution. The running time of these solutions through a capillary tube viscometer was determined and the limiting viscosity number  $[\eta]$  was calculated with the help of the Schulz–Blaschke formula (ISO 2004). The average DP of the cellulose and NFC samples was calculated from  $[\eta]$  using the Staudinger–Mark–Houwink equation (Gruber and Gruber 1981).

##### *Scanning electron microscopy (SEM)*

Cellulose raw materials and NFC suspensions were diluted with deionized water to 0.1 % (w/w) and mixed using the homogenizer. A drop of the diluted suspensions was placed onto a mica plate laminated

specimen holder. The samples were dried in vacuum and sputtered directly with a platinum layer of 8 nm (BAL-TEC MED 020 Modular High Vacuum Coating Systems, BAL-TEC AG, Lichtenstein). SEM images were recorded with a FEI Nova NanoSEM 230 instrument (FEI, USA) with an accelerating voltage of 5 kV and a working distance of 5 mm.

#### *Rheology of neat NFC suspensions*

Samples of NFC2 suspensions were taken for process monitoring during the fibrillation process after each pass through the grinder and after 2, 5, 8 and 10 passes through the interaction chambers of the high pressure homogenizer. NFC1 and NFC2 suspensions of 0.5, 0.75 and 1 % (w/w) were then further prepared for quality assessment after the fibrillation process by mixing them at 11,000 rpm using a homogenizer (Ultra-Turrax T25 digital, IKA Werke, Germany) for 3 min to achieve homogeneous dispersion. The resulting samples were degassed under vacuum to remove trapped air bubbles.

The rheological measurements were performed with a rotational rheometer with concentric cylinder geometry (Rheolab QC, CC39 geometry, 1.64 mm gap size, Anton Paar, Austria). The measurements were conducted at 25 °C in controlled shear rate mode by varying the shear rate from = 0.1 up to 1,000 and back to 0.1 1/s. A duplicate of each measurement was performed.

#### *Rheology of acrylate–NFC suspensions*

Acrylate–NFC suspensions were used as described above without further preparation. Measurements were done with a rotational rheometer with a higher measurable viscosity range compared to the rheometer used before (Physika MCR300, concentric cylinder CC27 geometry, 1.13 mm gap size, Anton Paar, Austria). The controlled shear rate experiments were done as described above. Each measurement was performed in duplicates.

#### *Storage stability of acrylate–NFC suspensions*

The storage stability of selected acrylate–NFC suspensions was evaluated by monitoring the viscosity during an accelerated storage experiment. Because of the lack of a standard method, an own method was set

up according to several suggestions found in literature (Koleske 2012). Acrylate–NFC suspensions with Acr2 and Acr3 and the corresponding neat NFC1 suspensions were tested. Sealed bottles with the suspensions were stored in a laboratory oven at 40 °C for 4 weeks. Rheological measurements as described before were done at the beginning and after each week during the accelerated storage. The suspensions were stirred slightly before measurement.

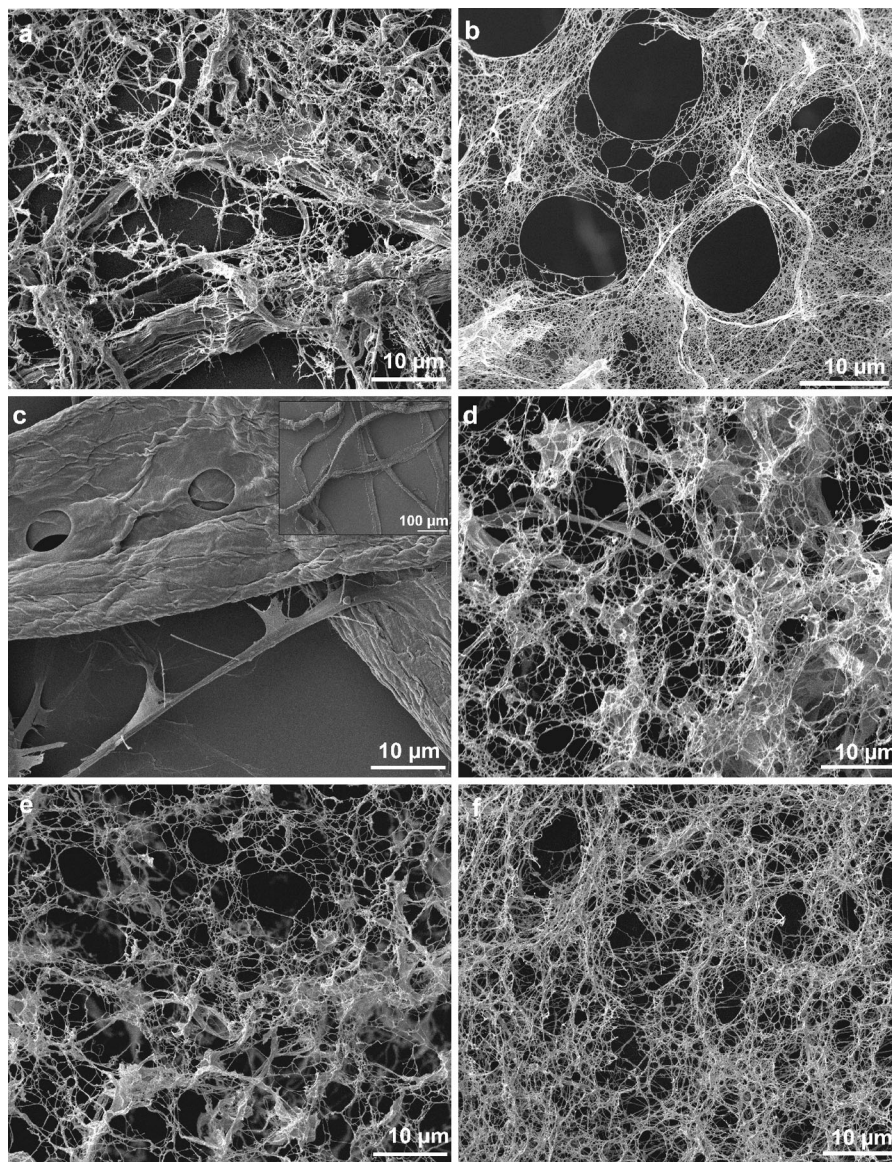
## **Results and discussion**

### *Fibrillation of cellulose raw materials*

Figure 2 shows SEM micrographs of the raw materials, intermediate products of NFC2 and the final NFC products. The beech wood pulp (Fig. 2a) was delivered already refined and therefore appeared as fibrillated material with fibre diameters in nm and  $\mu$ m range. After high pressure homogenization, the final NFC1 (Fig. 2b) was much finer than before fibrillation. In contrast, the softwood pulp (Fig. 2c) consisted solely of fibres with diameters in the  $\mu$ m range. It was therefore necessary to use a grinder in the first disintegration step to avoid clogging of the interaction chambers in the high pressure homogenizer. Figures 2d, e represent the softwood pulp after 7 and 10 grinding passes, where the fibres were strongly fibrillated compared to the initial fibre size. The fibrillation grade increased with the number of passes, but still occasional bigger fibres were noticed. During processing with the high pressure homogenizer, the fibres got finer (images not shown) and resulted in NFC2 (Fig. 2f), which showed the finest fibres and highest homogeneity among all disintegrated materials after the complete fibrillation process. Both NFC types built up the typical NFC network structure reported many times in literature (Klemm et al. 2011).

In addition to the visual evaluation, other methods were used to monitor the fibrillation quality. A common way to analyse NFC and their untreated raw materials is the determination of the degree of polymerization (DP). The DP of native celluloses is usually between 20,000 and 40,000, depending on the cellulose source. This initial DP is usually reduced by purification procedures to 2,500 and by regeneration processes to 200–400 (Nevell and Zeronian 1985). As already described in the very early papers on NFC, the





**Fig. 2** SEM micrographs of the cellulose raw materials and of the produced NFC: **a** refined beech wood pulp, **b** NFC1 after the mechanical disintegration process with inline dispersing system and high pressure homogenizer, softwood pulp before **c** and

after 7 (**d**) and 10 (**e**) passes through the grinder, **f** NFC2 after the complete disintegration process with grinder and high pressure homogenizer

DP usually decreases during the fibrillation process of cellulose by high pressure homogenization as well as by grinding (Herrick et al. 1983; Zimmermann et al. 2010). The determined DPs of the used cellulose pulps and NFCs presented in Table 3 are in good agreement with the literature. Both raw materials had their DP in a comparable range 1,440 for the beech wood pulp and 1,541 for the softwood pulp, respectively. This might be surprising, as the fibres looked far different, but

indeed it should be considered, that the DP is not directly correlated to the fibre length and diameter (Iwamoto et al. 2007). After processing, both NFC had decreased DP values compared to the starting materials, between 981 and 1,108 for NFC1 and between 1,059 and 1,113 for NFC2. For the softwood pulp, a stepwise decrease of the DP of the starting cellulose (1,541), to the grinded cellulose (1,292) and the final NFC2 (1,059 and 1,113) was apparent.

**Table 3** Degree of polymerization (DP) of cellulose raw materials and produced NFC

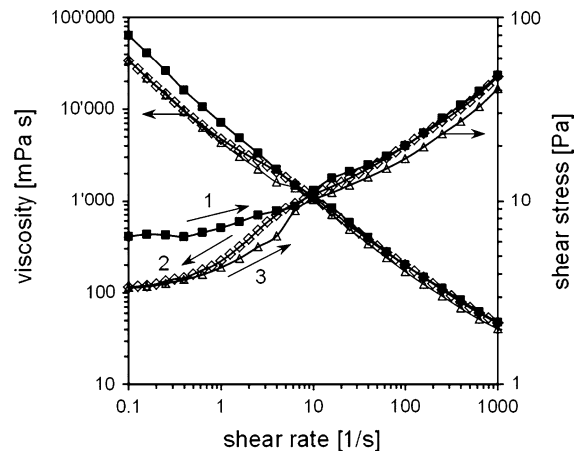
	DP	
	NFC1	NFC2
Raw material	1,440	1,541
After grinder	–	1,292
NFC (1st batch)	1,108	1,059
NFC (2nd batch)	981	1,113

Since the determination of the DP can be time consuming and laborious, rheology was chosen as additional method for process monitoring and quality assessment.

### Rheology of NFC suspensions

#### Flow curves of NFC suspensions

The general flow behaviour of the used NFC is discussed briefly, before going into details about using rheology measurements for process monitoring and quality assessment. Rotational measurements with controlled shear rate were conducted and a typical flow curve is given in Fig. 3 for the suspension of NFC1 at 1 % concentration. Rheology measurements of NFC2 resulted in similar flow curves. Measurements were done with both, increasing and decreasing shear rates. The flow curve of the NFC1 suspension shown in Fig. 3 exhibits a shear thinning behaviour, as already known from the very early works on NFC (Herrick et al. 1983). The flow behaviour in the upper shear region (above 10 l/s) does not depend on the flow history and direction of measurement. In the lower shear region, differences appear. The viscosity and especially the shear stress of the first measurement at increasing shear rates are augmented compared to the second (decreasing shear rate) and third (increasing shear rate) measurement. In addition, a small hysteresis is visible. A more distinct hysteresis was already described by Iotti et al. (2011). They described three network structures, a no-shear structure with a yield stress, a high shear structure with pure shear thinning behaviour above the hysteresis and a low-shear structure. This model fits well to the flow behaviour presented in Fig. 3. With increasing shear rate, the inner structure of the NFC suspension is broken down slowly, until the yield stress is reached.



**Fig. 3** Flow curves of NFC1 suspension at 1 % NFC content; (filled square) 1st measurement step after filling the sample into the cup from low to high shear rates, (open diamond) 2nd step from high to low shear rates, (open triangle) 3rd step from low to high shear rates

This is especially visible for the shear stress in measurement 1 of Fig. 3. The hysteresis represents the transition between the no- or low-shear region and the high shear region. A shear induced structure is formed. These results are in line with earlier, detailed investigations (Karppinen et al. 2012; Saarikoski et al. 2012; Björkman 2006). Karppinen et al. (2012) and Saarikoski et al. (2012) investigated the same shear regions by recording a movie of NFC suspensions while doing rheological measurements. Thereby, they could visualize the structural changes in the NFC microstructure. Björkman (2006) described the flow behaviour of concentrated fibre suspensions in general and set up the module suspension theory: he reduced suspension flocs to rectangular model flocs and stated that increased shear stress leads to a squeezing out of liquid from the flocs. In consequence, the shape of the model flocs change and flocs are separated into smaller module flocs. This structural change causes the flow behaviour observed in our experiments.

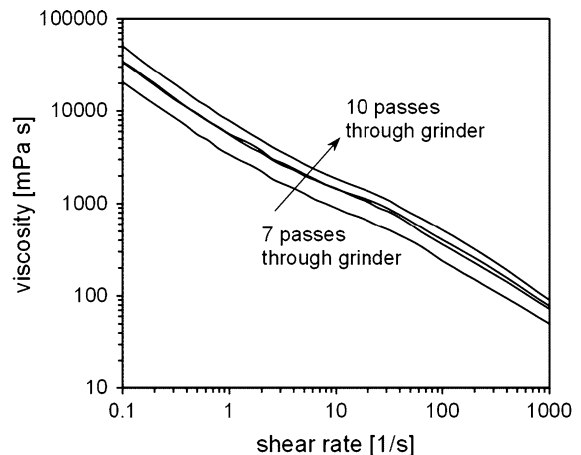
Additionally to the changing floc structure in the NFC suspension, the effect of wall slip or wall depletion on the flow chart should be considered. Wall slip is known to be present in two-phase systems, such as high molecular weight polymer solutions, particulate or flocculated suspensions, such as NFC suspensions, or even emulsions with large droplet sizes (Barnes 1995). The continuous phase enriches at the geometry boundary and forms a very thin layer

depleted of the dispersed phase. During shear, the real shear rate at the geometry boundary is higher than in the bulk of the suspension, which results in a lower measured viscosity than the real viscosity of the suspension (Saarikoski et al. 2012). This effect is emphasized more at decreasing measuring gap sizes in relation to the particle size and its impact on the measuring results is the highest at low flow rates. For this reason, this effect may also result in false thixotropy and false yield stress (Barnes 1995). Wall slip might be minimized or prevented by using a roughened measuring geometry, which was not used in our experiments. The measuring gap size of 1.64 mm was comparably large and according to Saarikoski et al. (2012) would therefore result in decreased floc size during shear. At least at higher shear rates, the adulterant effect of wall slip should be minimized due to the reduced floc size. Saarinen et al. (2014) additionally could visualize that when measuring above the yield stress, a slipping layer was present but the bulk of the suspension was also shared throughout the whole gap. For this reason, the comparison of different suspensions in the presented experiments was mainly done at high shear rates. Moreover, the viscosity measurement from high to low shear rate, which was independent from the sample history, was chosen for further comparisons over the whole shear rate range.

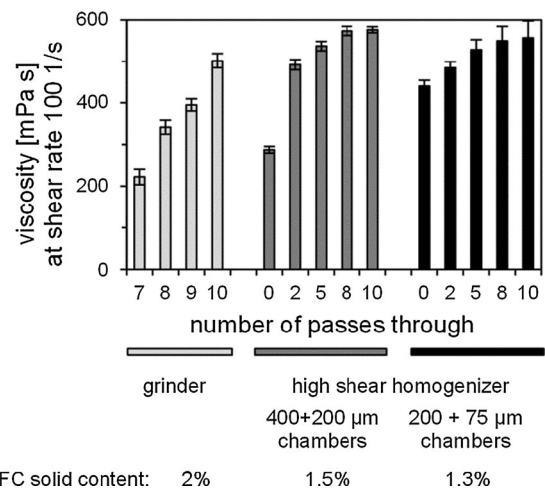
### Fibrillation monitoring

The fibrillation progress of the softwood pulp was monitored in detail with the help of viscosity measurements and results are presented in Figs. 4 and 5. Figure 4 displays the flow curves of the softwood pulp suspensions (NFC2) during the grinding process. Figure 5 contains the viscosity values at a fixed shear rate of 100 l/s during the whole fibrillation process. Measurements of the starting softwood pulp and of material which passed less than 7 times through the grinder were not possible to record. Based on an insufficient fibrillation, the fibres were still too long and resulted in inhomogeneous suspensions. The flow curves of these suspensions were very irregular and phase separation was observed.

Figures 4 and 5 show that each pass through the grinder and the high shear homogenizer led to a viscosity increase, as already described earlier by other groups (Saito et al. 2006; Lasseguette et al.



**Fig. 4** Flow curves of softwood pulp suspensions after 7, 8, 9 and 10 passes through the grinder at 1.8 % (w/w) concentration



**Fig. 5** Viscosity values at shear rate of 100 l/s of softwood pulp suspensions (NFC2) at different stages of the fibrillation process; the error bars correspond to the standard deviation of three replicates

2008; Saarikoski et al. 2012). It was apparent as well, especially for the fibrillation step with the high shear homogenizer that the viscosity increase levelled off after a certain number of passes. For both interaction chamber combinations, the viscosity changed only little after 5–8 passes. For example, while fibrillating within the 75 and 200 μm interaction chambers of the high shear homogenizer, the viscosity first increased distinctly from 440 to 485 (2 passes), 528 (5 passes) and 550 mPa s (8 passes) and finally only increased little to 557 mPa s after 10 passes. Therefore, process



optimization was possible and the number of passes through the high shear homogenizer could be reduced for the next fibrillation batches.

In Fig. 5 the increase in viscosity within one fibrillation step seems to be followed by a strong decrease while changing, e.g., from the grinding to the high shear homogenization process. This was due to varying cellulose concentrations during the different process steps and due to different sample histories prior to measurement.

Thus, NFC1 and NFC2 suspensions with defined cellulose solid contents and a reproducible preparation method were prepared at two different stages of fibrillation. The corresponding results are displayed in Fig. 6. The refined beech pulp, raw material of NFC1, exhibited the lowest viscosities at all three tested concentrations. The suspension with 1 % refined beech pulp content had a viscosity of 35 mPa s at 100 l/s. After the whole fibrillation process, the resulting NFC1 had eightfold higher viscosity values, 280 and 268 mPa s for a first and second batch of NFC1, respectively. Additionally taking into account the values of the suspensions at 0.5 and 0.75 % NFC

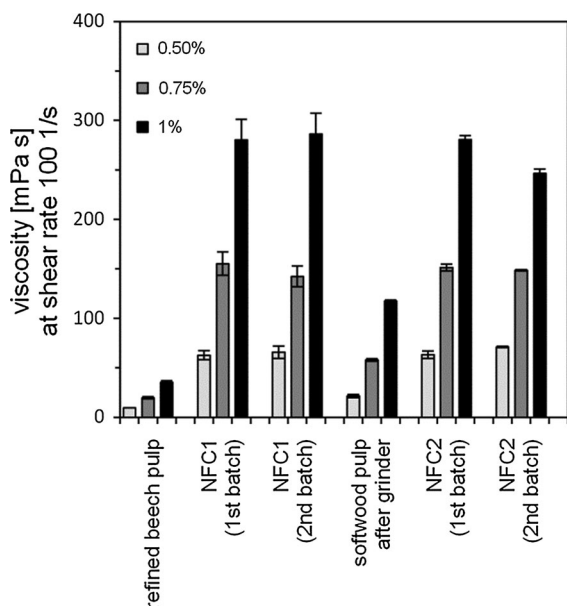
content, it is obvious that the viscosity measurements and thus the fibrillation were reproducible. Moreover, the viscosities of the NFC1 suspensions were also comparable to the corresponding results of NFC2. These values were in the same range, being 281 and 247 for the first and second batch at 1 % NFC2 content. It is remarkable, that the quality of the two NFC2 batches did not change significantly, although the number of fibrillation passes through the high pressure homogenizer was reduced to 8 instead of 10 as described above. Figure 6 also contains the viscosity values of the softwood pulp measured after the sole grinding process without high pressure homogenizer treatment. At 1 % solid content, the viscosity of this intermediate product was only 118 mPa s and therefore lower than the values of the final NFC2.

These results show that easy to handle viscosity measurements with a rotational rheometer are a convenient and also fast method to monitor and optimize the fibrillation process and to conduct quality control. These results were supported by SEM images of the same samples, where the changes in fibre dimensions could be visualized. Thus, the optimum number of passes through a disintegration device can be determined, which also helps, e.g., to save energy costs.

#### Preparation of acrylate–NFC1 suspensions

Only NFC1 was used for the preparation of the acrylate–NFC suspensions due to availability. Four different commercial acrylic polymer emulsions were selected, to cover a broad range of polymers with different properties. All of these polymer emulsions are typical binders for exterior wood coating applications. In general, waterborne emulsified polymers were used due to environmental reasons.

Formulation recommendations for fully functioning wood coatings, namely transparent stains, were provided by the suppliers of the polymer emulsions. For our own standard formulation, the components were reduced to a necessary minimum and the composition is summarized in Table 2. Suspensions with higher NFC concentrations than 0.91 % were hardly processible without any additional degassing. The viscosity of suspensions with higher NFC content became too high, so that air bubbles were trapped in the suspensions, which would have led to incorrect viscosity measurements.

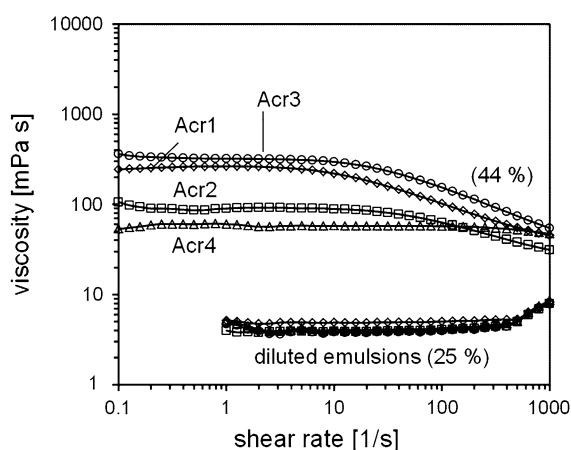


**Fig. 6** Viscosity values at shear rate of 100 l/s for NFC1 and NFC2 suspensions, suspensions of the starting refined beech pulp and the softwood pulp after grinding at defined concentrations of 0.5, 0.75 and 1 % NFC (w/w); the error bars correspond to the standard deviation of three replicates

## Rheology of acrylate–NFC1 suspensions

### Neat acrylate polymer emulsions

Figure 7 contains the flow curves of the acrylate emulsions at high solid content of 44 % and lower solid content of 25 %, which corresponds to the polymer content in the NFC–polymer suspensions and which will be discussed later. At 44 %, Acr1, Acr2 and Acr3 possessed shear thinning behaviour at higher shear rates and the Acr4 showed Newtonian flow behaviour over the whole measuring range. The values and flow characteristics differed from each other most probably due to different surface properties and modes of stabilization, which were not known in detail. At a reduced solid content of 25 %, flow curves of the different diluted emulsions were similar to each other, although these acrylates had different flow behaviours at the initially higher solid contents (Fig. 7). The viscosity was decreased compared to the undiluted emulsions and exhibited Newtonian flow behaviour. At 25 % solid content the polymer emulsions were diluted so much that interactions between the emulsion particles, which would promote non-Newtonian behaviour, were prevented and therefore Newtonian flow curves were measured. Interestingly, the viscosity was more or less the same for all acrylates and only a little higher than the viscosity of pure water at 25 °C (0.89 mPa s). Only the viscosity of Acr1 was slightly higher.



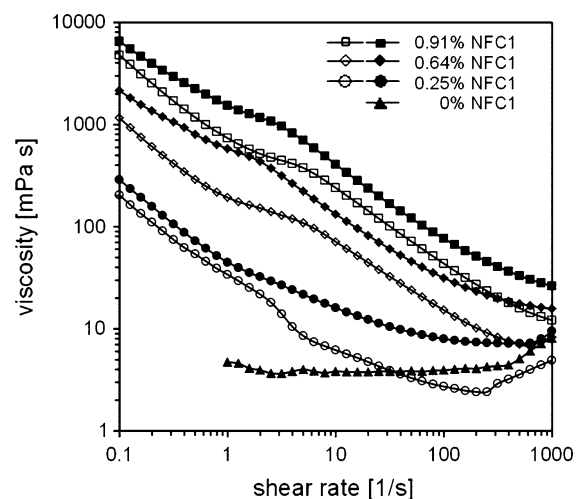
**Fig. 7** Flow curves of the four neat acrylate polymer emulsions at 44 % solid contents and diluted emulsions at 25 % solid content; symbols of diluted emulsions correspond to the ones of neat emulsions

The increase of viscosity in the upper end of the measuring interval is assumed to be due to turbulences, which are common for low viscosity liquids at high shear rates (Mezger 2011).

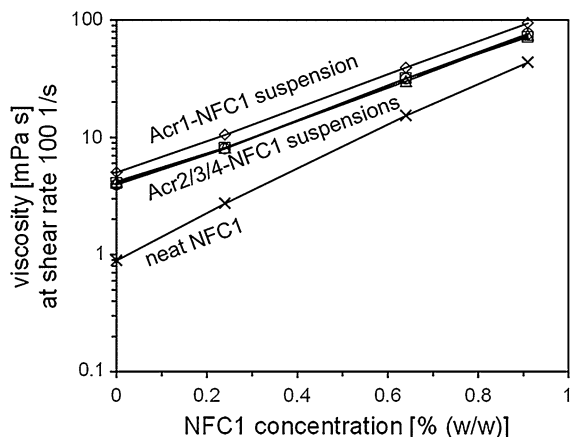
### Acrylate–NFC1 suspensions

The addition of NFC1 to the diluted acrylate suspensions led to an increase in viscosity and changed the general flow behaviour. Figure 8 shows exemplarily the flow curves of all Acr2–NFC1 suspensions and of neat NFC1 suspensions at the same concentration. It is obvious, that the general flow behaviour changed from Newtonian flow (diluted acrylate emulsions) to shear thinning flow (acrylate–NFC1 suspensions). Furthermore, the viscosity increased with increasing NFC1 concentration, e.g. from 3.9 (0 % NFC1) to 8.0 (0.25 % NFC1), 31.5 (0.64 % NFC1) and 76.4 mPa s (0.91 % NFC1) at the fixed shear rate of 100 1/s. At this point, the viscosity increased by a factor of nearly 20. The correlation between NFC1 concentration and viscosity at 100 1/s is further depicted in Fig. 9. A linear increase of the viscosity on the logarithmic scale after NFC1 addition is visible. Consequently, the viscosity of acrylate–NFC1 suspensions is exactly tuneable in the considered shear range by NFC1 addition.

Besides the flow curves of the acrylate–NFC1 suspensions, Figs. 8 and 9 also contain the values of



**Fig. 8** Flow curves of Acr2–NFC1 suspensions (filled symbols) at different NFC1 concentrations and corresponding neat NFC1 suspensions (empty symbols)



**Fig. 9** Viscosity values of acrylate–NFC1 suspensions and neat NFC1 suspensions at shear rate of 100 l/s depending on NFC concentration

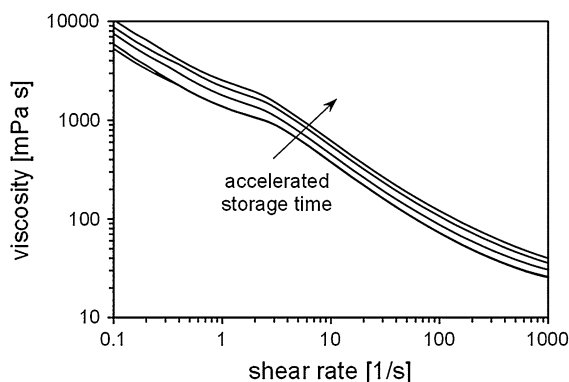
neat NFC1 suspensions at the corresponding concentrations. Since sample preparation has a big impact on the viscosity, we ensured comparable viscosity measurements by preparing neat NFC1 suspensions and acrylate–NFC suspensions the same way. The general flow characteristics of both suspensions were comparable. They were shear thinning and in both cases the viscosity increased with higher NFC1 content. However, the viscosity values of the acrylate–NFC1 suspensions were always higher than those of the corresponding neat NFC1 suspensions. We suppose that the higher solid content in the suspension and interactions between NFC1 and acrylate particles were responsible for these results. Nevertheless, the influence of the acrylic polymers on the flowing properties of the acrylate–NFC1 suspensions was very low and the characteristics of NFC1 were predominant. This result was underlined by the fact that curves and viscosity values of the acrylate–NFC1 suspensions were nearly independent from the type of acrylate and its initial flow behaviour (compare Fig. 7). Again, only Acr1 exhibited higher values, which was neither explainable nor further investigated.

The viscosity change after addition of NFC1 to acrylate emulsions is comparable to conventional thickeners and rheology modifiers. Nowadays, such thickeners are mainly used in paint and coating formulations to adjust coating consistency in the so called mid-shear region (10–1,000 l/s), the main shear region for coating processing (Koleske 2012). The increased viscosity due to NFC1 addition in the low

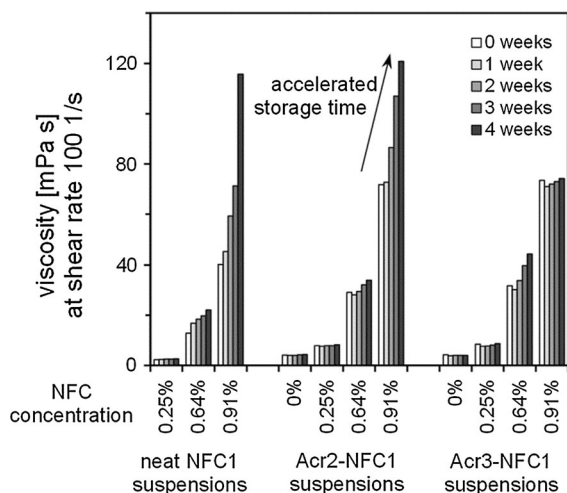
shear region (less than 10 l/s), which describes the coating at rest, seems to be favourable. High viscosity in this region prevents for instance pigment settling during storage or sagging of the coating on vertical surfaces (Molenaar 1997). The impact of NFC1 addition to the high shear region (more than 1,000 l/s), which describes the coating properties during application, e.g., brushing or spraying, was not further investigated. Anyway, the desired flowing properties in the three regions are always related to the application and vary depending on the raw materials of a coating composition. It should also be considered, that we used neat polymeric binder materials with only few additives to investigate the sole impact of NFC addition. Ready-to-use wood coatings also contain other components such as  $\text{TiO}_2$  as a white pigment or silicates for improving the mar-resistance (Wicks et al. 2006). These additives, which were not used in this study, will affect the coating rheology themselves and might even affect it due to interaction with the NFC.

#### Accelerated storage stability of acrylate–NFC1 suspensions

The stability of acrylate–NFC1 suspensions was evaluated by monitoring the viscosity during accelerated storage for the period of 4 weeks at 40 °C in a laboratory oven. Results of these viscosity measurements are presented in Figs. 10 and 11. Figure 10 shows the viscosity change during the accelerated storage of the Acr2–NFC1 suspension with 0.91 % NFC1 concentration. The general flow behaviour was not affected during storage, but the viscosity



**Fig. 10** Flow curves of Acr2–NFC1 suspension with 0.91 % NFC1 during accelerated storage for 4 weeks at 40 °C



**Fig. 11** Development of viscosity values during accelerated storage of selected acrylate–NFC1 suspensions with Acr2 and Acr3 and as reference neat NFC1 suspension at shear rate of 100 1/s

increased. The results of all tested suspensions are summarized in Fig. 11. The viscosity of suspensions with NFC1 content of 0.25 % or without NFC1 did not change significantly. Suspensions with higher NFC1 contents generally exhibited increased viscosities after storage as already described for the Acr2–NFC1 suspension with 0.91 % NFC1. Only the viscosity of the Acr3–NFC1 suspension with 0.91 % NFC1 content kept constant after storage. This deviating result was not further investigated.

No appropriate literature was found to explain the viscosity increase of NFC-suspensions during storage at increased temperatures. Several, speculative aspects might be considered to explain these observations. On the one hand, the interfibrillar interaction might be increased due to more entanglements and hydrogen-bonds between single fibrils. Such increased interactions would increase the resistance to flow and therefore the viscosity of a suspension.

On the other hand, swelling of the NFC might be a reason. Swelling is very well reported for native dried and never-dried cellulose, dry NFC films and composites containing NFC, but not for suspended NFC (Eyholzer et al. 2011; Ahola et al. 2008; Spinu et al. 2011). In general, water diffuses into the amorphous part of cellulose and causes swelling of the entire material (Aulin et al. 2009). Swelling of NFC fibrils followed by increased NFC floc size might be

explained with the time and temperature dependence of diffusion and with size effects. Fick's second law of diffusion includes the time dependence of diffusion and according to the Einstein relation, the diffusion coefficient depends on the temperature (Atkins and De Paula 2006). The diffusion coefficient increases with increasing temperature, which could explain additional swelling of NFC due to accelerated diffusion at the higher storage temperature (40 °C). In addition, the diffusion of water is enhanced by the increased fibre surface compared to the fibres before fibrillation. Such phenomena were already described for wood pulp fibres in 8 % NaOH solutions at low temperatures (Spinu et al. 2011). In that study, highly fibrillated fibres swelled much faster compared to larger fibres and at lower NaOH concentrations, only the fibrillated fibres swelled.

Both discussed aspects, interfibrillar interaction and swelling, need to be proved by further investigations, as they are only speculative.

The main conclusion of this accelerated storage experiment with regard to the coating application is, that although the viscosity slightly increased, the general flow behaviour did not change. Hence, from a practical point of view, a potential paint or coating containing NFC would need to be diluted accordingly after long time storage. Afterwards, the same flowing characteristics would be obtained again.

## Conclusion

Nanofibrillated cellulose (NFC) was disintegrated from two different cellulose raw materials by using adapted fibrillation processes depending on the initial fibre size. Rheological measurements were found to be a convenient and also fast method for fibrillation process monitoring (quality control) and subsequent optimization.

In a second step, the viscosity of water-borne acrylate–NFC suspensions was investigated with regard to a potential use of NFC in coating compositions. The flow characteristics of the NFC were dominating the acrylate–NFC suspensions and the type of polymer was of minor importance for the rheological behaviour of the tested suspensions. The viscosity increased exponentially due to NFC addition. Consequently, the viscosity of acrylate–NFC suspensions is precisely adjustable and predictable in



the considered shear range by NFC addition. The general flow behaviour of the acrylate–NFC suspensions remained the same during accelerated storage at elevated temperatures. Possible explanations of the increasing viscosity of NFC and acrylate–NFC suspensions under the influence of temperature and time might be increased interactions between single fibrils within the network and/or swelling of the NFC due to increased water diffusion and increased fibre surface. Both impacts might increase the resistance to flow and therefore the suspension viscosity.

The study shows that rheology is an important issue that has to be taken into account when applying NFC as additive in water based coating systems and that NFC is suitable as component for coating applications.

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